

DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE No. 79

FLUORSPAR

[All results are based on a sample dried for one hour at 105 to 110° C.]

ANA- LYSTS*	CaF ₂		CaCO ₃		SiO ₂	Zn	Pb	S	Fe ₂ O ₃	Al ₂ O ₃	MgO	BaO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	MnO	
	Bureau of Stand- ards method	Other meth- ods ^c	Calcu- lated from direct deter- mina- tion of CO ₂	Based on cal- cium leached from sample by di- lute acetic acid	Bureau of Stand- ards method													
1	{94.93 ^b 94.89 ^e }		2.28		1.90 ^d	0.34	0.24	0.13	0.14	0.03	0.16	0.08	0.06	0.01	0.004	0.003	0.003	
2	94.88 ^b		2.24		1.87	.35	.23	.13	.16	.01	.11	.07	0.10		.005	.003	.003	
3	94.77		2.19	2.09	1.95	.34	.23	.12				.05						
4	94.77	94.71 ^c	2.29		1.90	.32	.25	.16	.18		.13	.07	.06					
5	94.99	94.97		1.83	1.84	.34	.23	.10										
6	94.77		2.25	2.27	1.93			.13										
7	94.72	94.80	2.30	2.00	1.80			.14										
	94.89	94.94		1.96	1.70			.12										
	94.96	94.90	2.26		1.89	.35	.22	.13				.08						
10	94.94	94.73	2.20	2.23	1.95	.36	.22	.13				.07						
11	94.89	94.85	2.21	2.22	1.95		.20		.34			.04						
12	94.90	94.80	2.09	2.16	1.96	.37	.27		.18									
13	94.77	94.67	2.14		1.86	.34	.24	.12	.31			.08						
14	94.71	94.64		2.15	{1.88 1.82}			.12										
Averages	94.85	94.80	2.22	2.10	1.88	.35	.23	.13	.15	.02	.13	.07	.06	.01	.005	.003	.003	
General Averages	94.83		2.17 ^h		1.88	.35	.23	.13	.15	.02	.13	.07	.06	.01	.005	.003	.003	

* The results in this column are those found by the method regularly employed in the analyst's laboratory.
^b Finished by weighing as CaO.

^c Finished by titrating CaC₂O₄ with KMnO₄.
^d By the use of a method in which the fluorine was removed before the determination of silica an average of 1.77 per cent was obtained.

^e Peroxide fusion.
^f Bethlehem Steel Co.'s method.
^g Eschka's method.
^h Recommended value=2.25 per cent.

The results shown above, unless otherwise stated, were obtained by the methods outlined on this certificate or by slight modifications. As the methods for CaF₂, SiO₂, and CaCO₃ are more or less empirical, the directions must be carefully followed in order to duplicate results. It is believed that the certified percentage of CaF₂ is accurate to ±0.25 per cent and that for SiO₂ to ±0.15 per cent.

There is no certainty as to how the elements exist in combination in this sample. Lead might exist as sulphide, carbonate, or fluoride. It was, therefore, deemed advisable to list lead, zinc, and sulphur as the elements and the other minor constituents as oxides although it is not at all certain nor probable that they exist as such. Tests have shown that all but 0.01 per cent of the sulphur is present as sulphide.

Analysts Nos. 1 and 2 found a trace of copper (0.002 and 0.006 per cent of CuO, respectively).

*LIST OF ANALYSTS

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| <ol style="list-style-type: none"> 1. James I. Hoffman, Bureau of Standards, Washington, D. C. 2. W. F. Muehlberg, chief chemist, Newburgh Steel Works, Cleveland, Ohio. 3. F. G. Kelly, chief chemist, Tennessee Coal, Iron & Railroad Co., Ensley, Ala. 4. Frederick Wynkoop, Booth, Garrett & Blair, Philadelphia, Pa. 5. George P. Vanier, chief chemist, Bethlehem Steel Co., Steelton Plant, Steelton, Pa. ^a S. B. Benzing, chief chemist, Bethlehem Steel Co., Lebanon Plant, Lebanon, Pa. E. Steiner, chief chemist, Bethlehem Steel Co., Cambria Plant, Johnstown, Pa. | <ol style="list-style-type: none"> 8. W. F. Lantz, chief chemist, Bethlehem Steel Co., Bethlehem Plant, Bethlehem, Pa. 9. C. E. Nesbitt, chief chemist, Carnegie Steel Co., Edgar Thomson Works, Braddock, Pa. 10. H. E. Campbell, chief chemist, Carnegie Steel Co., Clairton, Pa. 11. W. D. Brown, chief chemist, Carnegie Steel Co., Duquesne Works, Duquesne, Pa. 12. J. L. Harvey, chief chemist, Carnegie Steel Co., Munhall, Pa. 13. L. P. Chase, chief chemist, Illinois Steel Co., South Works, Chicago, Ill. 14. N. M. Randall, chief chemist, Bethlehem Steel Co., Maryland Plant, Sparrow's Point, Md. |
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Washington, D. C.

September 21, 1929

George K. Burgess

Director

METHODS OF ANALYSIS

1. FINENESS OF THE SAMPLE

The sample should be ground to pass a No. 80 sieve. Coarser material has a tendency to decrepitate on ignition.

2. **Drying.**—Fluorspar offers little difficulty in drying or weighing the sample. A sample dried for one hour at 105° to 110° C. is satisfactory.

3. **Carbonates.**—Determine CO₂ by evolving it with dilute HCl (1:1)¹ and absorbing it in ascarite. Less attack on the flask results if H₃BO₃ is also used. If desired, the CO₂ may be absorbed in Ba(OH)₂ and determined by titration. Report as "total carbonates as CaCO₃."

The apparatus consists of a flask fitted with a small reflux condenser which is followed by bulbs or tubes containing (1) H₂SO₄, (2) pumice impregnated with anhydrous CuSO₄,² (3) "dehydrite" (Mg(ClO₄)₂ · 3H₂O), (4) a weighed tube containing ascarite and "dehydrite" and (5) a protecting tube containing "dehydrite." All connections are made by simple mercury seals. P₂O₅ may be used instead of "dehydrite." Dilute HCl (1:1) containing 1 g of H₃BO₃ per 100 ml was used in the evolution of the CO₂.

A determination of CO₂ by heating the sample in a combustion tube would include organic carbon and possibly a little SiF₄.

4. **Silica.**—Transfer a 1.000 g sample to a 50-ml beaker, add 3 ml of acetic acid-bromine mixture,³ cover the beaker, and digest on the steam bath for 10

¹ Prepared by mixing 50 ml of the concentrated acid with 50 ml of water. This system of designating dilute acid is used throughout. For example, dilute HCl (5:95) denotes a solution containing 5 ml of the concentrated acid and 95 ml of water. If no dilution is specified, the concentrated reagent is intended.

² Prepared by saturating pumice with a solution of CuSO₄, drying and heating at 150 to 160° C. for four to five hours.

³ Add 20 ml of liquid bromine to 80 ml of glacial HC₂H₃O₂ and mix thoroughly. If liquid bromine comes in contact with the skin, painful burns will result which can be checked and relieved by quickly immersing and thoroughly rubbing the wound in carbon tetrachloride, and then allowing it to dry. The evaporation of the tetrachloride carries with it the free bromine.

⁴ A 20 per cent solution of KBr saturated with Br₂. Transfer 500 g of Br to a liter bottle, add 700 ml. of a 20 per cent solution of KBr, and cautiously shake. When the solution is exhausted, more of the 20 per cent solution of KBr may be added.

minutes. Next add 10 ml of water and 10 ml of potassium bromide-bromine mixture⁴ and digest for 40 minutes. Finally add 5 ml of a 50 per cent solution of NH₄C₂H₃O₂ and digest for 10 minutes. Add a little paper pulp and filter on a paper of close texture. Wash with 30 to 40 ml of hot water, ignite in platinum at approximately 650° C., cool in a desiccator, and weigh. Treat with about 3 ml of HF, break up the lumps or cakes with a platinum rod, and evaporate to dryness. Repeat the treatment with HF, ignite at approximately 650° C. for about five minutes; cool, and weigh. The difference between the two weights is to be regarded as silica. Owing to the possible retention of some lead and zinc, the temperature of ignition should be rather closely controlled. This can be conveniently done in a muffle furnace.

5. **Calcium fluoride.**—Transfer 0.5000 g of the sample (dried at 105° to 110° C.) to a 30-ml platinum crucible, add 15 ml of 10 per cent HC₂H₃O₂ and digest on steam bath for one-half hour, stirring with a glass rod at 5-minute intervals. Filter through a 7-cm filter paper of close texture and thoroughly wash the crucible and paper with small portions of hot water, using about 35 ml in all. Transfer the paper and precipitate to the crucible, dry, and ignite at a dull red heat.

Treat the residue in the crucible with about 3 ml of HF and evaporate to dryness. Add 1 to 2 ml of H₂SO₄ and evaporate to dryness under the hood. Cool, wash down the inside of the crucible with 1 ml more of H₂SO₄ (in order to catch any undecomposed particles of calcium fluoride), and again evaporate to dryness. Two or three evaporations with 3 to 4 ml of a 60 to 70 per cent solution of HClO₄⁵ may be substituted for the evaporation with H₂SO₄. Cool the crucible and immerse it in a beaker containing 150 ml of dilute HCl (5:95). Warm gently and remove the platinum crucible being sure to cleanse it from adhering particles of CaSO₄.

⁵ If HClO₄ is used, a few drops of HNO₃ should be added to oxidize any reducing substances before the HClO₄ starts to fume. Otherwise violent reactions may ensue.

Boil the contents of the beaker for 10 minutes, and 7 insoluble matter remains, filter, wash, and ignite residue in platinum.⁶

Pass H₂S into the clear filtrate for a few minutes and then make the solution ammoniacal. Continue the current of gas for 10 minutes and allow the precipitate to settle for 20 to 30 minutes. Filter and wash with NH₄Cl—(NH₄)₂S solution.⁷

Neutralize the filtrate and washings with HCl, add 20 ml of the acid in excess, and boil for two to three minutes to expel most of the H₂S. Add KBr—Br₂ solution⁸ until the solution remains yellow, boil until the finely divided sulphur has been oxidized, and continue the boiling until the bromine has been expelled. Filter if sulphur or sulphides are not removed by the treatment with bromine. Precipitate the calcium in the filtrate in a volume of about 200 ml by adding 2 g of (NH₄)₂C₂O₄·H₂O and then NH₄OH slowly and with stirring until the solution is slightly ammoniacal. Heat on the steam bath for one-half to one hour, stirring occasionally, cool to room temperature, and filter on a paper of close texture. Wash with a cold 0.1 per cent solution of (NH₄)₂C₂O₄·H₂O, ignite to constant weight, and calculate the CaO to CaF₂ (factor=1.392). The determination may be finished by titrating the calcium

ate with a standard solution of KMnO₄. In this case filter through a platinum or asbestos pad, finally wash the CaC₂O₄ with three or four 10-ml portions of cold water, and titrate as usual. To the CaF₂ found should be added 0.20 per cent to allow for the fluoride dissolved by the HC₂H₃O₂ and this result then corrected in accordance with the results obtained in a blank carried through all steps of the determination.

The use of platinum crucibles for the initial digestion with HC₂H₃O₂ obviates the quantitative transfer of the residue to the paper, and this saves time and keeps the volume of the washing solution at a minimum. Digestion can, however, be carried out in small glass beakers.

⁶ This residue may consist of BaSO₄, PbSO₄, or undecomposed CaF₂. Owing to the small size of the sample originally taken, it is not advisable to determine lead and barium at this point. The residue should be treated, however, with a few drops of HF and H₂SO₄, heated until these are expelled, digested with 1 to 2 ml of HCl on the steam bath, and the solution added to the main solution for the determination of calcium. If the original material contains much barium, more or less BaSO₄ separates but this is of no consequence.

⁷ Prepared by passing a moderate stream of H₂S for five minutes through a solution containing 5 ml of NH₄OH and 10 g of NH₄Cl per liter.

⁸ A 20 per cent solution of KBr saturated with Br₂. See method for silica. The addition of KBr—Br₂ solution soon after acidification is more efficacious in removing sulphur than it would be if the boiling were continued until sulphur coagulated and the KBr—Br₂ then added.

A small rod just a little longer than the depth of the crucible is very convenient to use in stirring the solution during the digestion and to pour against as the solution is transferred from the crucible to the paper.

After the treatment with HC₂H₃O₂, particles of the residue adhere to the surface of the crucible near the rim. These should be brushed to the bottom of the crucible with a piece of moist filter paper.

Sulphur is removed before calcium is precipitated, because sulphite or sulphate is formed when calcium oxalate containing sulphur is ignited, and in large precipitates these can not be entirely decomposed even by strong ignition. Results would consequently be high. Removal of sulphur is not needed if titration is to follow.

6. Sulphur.—Mix 1.000 g of the sample in a platinum crucible with 10 g of K₂CO₃ and 0.5 g of KNO₃, place the covered crucible in the muffle of an electric furnace, and heat until the mass is completely fused and the melt is quiet. An alcohol or petroleum ether flame may be used if an electric muffle is not available. When fusion is complete, gently rotate the crucible so that the cooling melt will solidify in a layer on the walls. Place the cooled melt in a beaker containing 150 ml of warm water, digest on the steam bath, and stir occasionally.

When the melt is disintegrated, filter and wash the residue thoroughly with small portions of hot water. Acidify the filtrate with HCl and add 20 to 25 ml of HCl in excess. Evaporate to dryness, wash down the inside of the beaker, again add 20 to 25 ml of HCl, and evaporate to dryness. Dissolve the salts in 100 ml of dilute HCl (2:98), filter, wash with hot water, and add 5 ml of a 5 per cent solution of BaCl₂·2 H₂O to the filtrate, which should have a volume of approximately 150 ml. Boil for 10 to 15 minutes, allow to stand for four hours or preferably overnight, filter, wash with hot water, ignite, and weigh as BaSO₄. A blank on the reagents should be carried through all steps of the method.

7. Barium.—Transfer 5.00 g of sample to a platinum dish and digest on the steam bath for 10 minutes with 10 ml of HF. Then add 5 ml of HNO₃ and 25 ml of 60 to 70 per cent HClO₄ and evaporate to dryness. Again add 25 ml of HClO₄ and evaporate to dryness. Repeat the addition of HClO₄ and again evaporate.

Take up the dry mass in 50 ml of dilute HCl (1:9) and heat to boiling. If a residue remains, filter, wash with warm water, ignite at as low a temperature as possible, and treat with 5 to 10 ml of HF and 5 to 10 drops of H₂SO₄. Expel the acids at a low temperature, fuse with about 1 g of Na₂CO₃, and extract the melt with water. Filter, wash the paper and residue with hot water, dissolve the residue in HCl, avoiding more than a few drops in excess, and add the clear solution to the main one. Dilute the combined solutions to 200 ml, heat nearly to boiling, and add dropwise and with stirring 4 ml of dilute H₂SO₄ (1:3). Boil for 15 minutes and digest on the steam bath for three to four hours. Do not allow the solution to cool below 40° to 50° C., because of the tendency of CaSO₄ to separate. If a precipitate forms, filter, wash with hot dilute HCl (1:99), and then with cold water. Ignite the precipitate and weigh as BaSO₄.

If lead is present in appreciable amount, the BaSO₄ may be contaminated by PbSO₄. To correct for this, add 5 ml of a 20 per cent solution of NH₄C₂H₃O₂ to the weighed precipitate, digest on the steam bath for 30 minutes, filter, and wash with hot water. Add a few drops of HCl to the filtrate, treat with H₂S, and if any PbS forms, remove it by filtration, cautiously ignite it at a dull red heat, treat with a few drops of HNO₃ and H₂SO₄, and again ignite at a dull red heat. Subtract the weight of PbSO₄ here found from that of the mixed sulphates and calculate the percentage of BaO or BaSO₄. A corresponding correction should also be made in the subsequent determination of lead.

8. Lead.—Pass H₂S for a few minutes into the filtrate obtained in the barium determination and then render the solution slightly ammoniacal. Continue the current of H₂S for 10 minutes and allow the solution to stand at the side of the steam bath for 30 minutes. Filter, wash a few times with NH₄Cl—(NH₄)₂S solution, and discard the filtrate. Dissolve the precipitate in 25 ml of hot dilute HNO₃ (1:2), dilute the solution, and repeat the precipitation and washing in order to eliminate all calcium which might otherwise be precipitated with the lead. Dissolve the precipitate in HNO₃ as before, add 3 ml of H₂SO₄, and evaporate until dense fumes of the acid appear. Cool, dilute with water to 50 ml, and allow to stand for three hours or over night. Filter, wash a few times with cold dilute H₂SO₄ (1:20), ignite the precipitate very cautiously to dull redness

(preferably in a muffle or radiator), and weigh as PbSO₄. If the sulphate was caught on paper instead of ash, the ignited residue should be treated with HNO₃ and H₂SO₄ before the final ignition.

The filtrate from the PbSO₄ may contain a trace of lead. To recover this and to free the solution from platinum before zinc is determined, adjust the acidity by neutralizing with NH₄OH and then adding 2 ml of H₂SO₄ per 100 ml of solution. Treat with H₂S, and if a precipitate forms, filter, wash, and cautiously ignite the residue at a low temperature. Treat with a few drops of H₂SO₄ and HNO₃, again ignite at a very dull red heat, and weigh. Add 5 ml of a 20 per cent solution of NH₄C₂H₃O₂, allow to stand on the steam bath for 30 minutes, filter, ignite in the same crucible, and again weigh. The difference between the two weights represents PbSO₄ which should be added to that already obtained. This correction is usually so small that it need not be made except in very accurate work. The treatment with H₂S in acid solution, however, should be made to remove the trace of lead and the varying amounts of platinum which may be present. Otherwise these would subsequently contaminate the zinc.

9. Zinc.—After having removed lead and platinum, boil the filtrate to remove H₂S, add methyl orange, carefully neutralize the solution, and then add enough H₂SO₄ to make the solution 0.01 N. If iron or aluminum are present in large amounts, they must be removed before the acidity is adjusted, for otherwise they will be precipitated in part. Pass a stream of H₂S through the cool solution for 30 minutes, allow to stand for one hour, filter on a paper of close texture, and wash with cold water. Ignite at a low temperature until the carbon of the paper is gone and then at a dull red. Weigh as ZnO.

10. Other Constituents.—Alkalies may be determined by the J. Lawrence Smith method. The other oxides can be determined by the usual procedures after fluorine has been volatilized by fuming with H₂SO₄ or HClO₄.

For a full discussion of these methods see "The Analysis of Fluorspar," by G. E. F. Lundell and J. I. Hoffman, Research Paper No. 51, B. S. Jour. of Research, 2, p. 671; 1929.